

## Fabrication and investigation of superhydrophobic surface by dip coating

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The present research work is focused on to fabricate and examine the characteristics of a superhydrophobic surface on copper (Cu) substrates by dip coating method. Three different samples of 'Cu' are set with chemical etching, mechanical rubbing and the combination of above two methods. The variations in the exterior surface morphologies have been examined by profilometer, scanning electron microscope and energy-dispersive X-ray spectroscopy. The adapted samples are immersed in a solution of silver nitrate follow by immersing in a combination of ethanol and perfluorodecyltriethoxysilane for 10 min. The presence of leaf and dendrites assemblies have been observed on the surface, which are useful to trap the air between them and the entrapment allows water to roll off from the surface. The outcomes reveal that the modified substrates have a water contact angle (WCA) of 159° in the case of 'Cu' using combination of chemical etching and mechanical rubbing followed by immersion coating. The proposed methodology has the advantage of size compatibility and easy scale up for the development of superhydrophobic surface on copper in a cost and time effective manner.

**Keywords:** Dip-Coating, Dendrites, Etching, Microstructure, Superhydrophobic Surfaces

The properties of metals, such as roughness and wettability, are modified by forming a hydrophobic/superhydrophobic film over the surface. The super hydrophobic external usually states that mixture of the static contact angle (CA) 150° and above with a CA hysteresis lesser than 5°<sup>1-3</sup>. It is categorized into 2 kinds conferring to water rolling angle; an enormously adhesive superhydrophobic exterior that allows water dewes to stick to the surface, even when the surface is twisted inverted and a lesser amount of adhesive superhydrophobic exterior with a progressing angle less than 5°<sup>4</sup>. The physical characteristics of superhydrophobic exterior have been examined, since the last span due to its beneficial topographies<sup>5</sup>. Different grades of aluminum (Al) and copper (Cu) are widely used as a base material in various industrial applications for the fabrication of system components and creating these exterior surfaces into superhydrophobic would essentially valuable, in terms of augmenting the system performance along with extended durability. Investigation on superhydrophobic exterior have shown a substantial development and many approaches have been effectively developed for the creation of superhydrophobic exterior on a variety of metal substrates<sup>6</sup>. However, many of the proposed methods possess certain limitations like complex

process controls, severe operating environments, requirement of special equipment and time consuming. Also, a lot of practical hankerings are present in the exiting methods to progress a superhydrophobic exterior on a substrate having larger surface area and complex geometry<sup>7</sup>. The collected works relating to the progress of superhydrophobic exterior are studied and presented as follows; Qian and Shen reported maximum water contact of 156° in 'Al' substrate by chemical etching method<sup>8</sup>. The creation of floret like arrangements on the 'Cu' substrate by one step deposition procedure changed 'Cu' into superhydrophobic exterior with a CA of 153±2°<sup>9</sup>. Yin *et al.* projected the mixture of anodic oxidation, limited etching and immersing in oxosilane for the progress of superhydrophobic exterior in an 'Al' substrate and stated an enriched corrosion inhabitation owing to the occurrence of crashes and the stable superhydrophobic coverings<sup>10</sup>. Lathe and Rao recounted a water contact angle of 163±2° and roll-off angle 5±1° in the cut-glass substrate with coating through using sol-gel resulting SiO<sub>2</sub> micro-particles<sup>11</sup>. The conversion from hydrophilicity to superhydrophilicity and superhydrophobicity was attained in 'Al' alloy by acid etching followed by the coating with polypropylene<sup>12</sup>. A new technique to provide

superhydrophobicity on 'Cu' piece was established by the mixture of chemical etching and polydimethyl silaxane template that give rise to CA and sliding angle of  $152^\circ$  and  $8^\circ$  respectively, even after it unprotected to sever moist conditions<sup>13</sup>. Numerous procedure have been applied to prepare superhydrophobic exterior on different substrates<sup>14-22</sup>. From the collected works it is clear that the projected approaches comprise complex procedure with more time consuming and only limited approaches have been stated for the progress of superhydrophobic exterior at micro/nano scale. Considering the interesting features of superhydrophobic exterior and the demanding need to progress a cost effective coating technique, an attempt is made in the present work to develop a superhydrophobic surface on 'Cu' substrates over a new method by combining chemical etching and mechanical rubbing followed by dip coating. The surface characterizations such as morphological study, chemical composition, roughness and water contact angle were analyzed and reported.

Dip coating methods offer the potential benefits of mild reaction conditions, easily tunable coating thickness up to micrometer and generally easier implementation in sequential making lines. Additionally, this process can be effortlessly applied to covering an adsorbent layer with complex geometries, maintaining a uniform thickness. It has the fascinating features of providing great potential to scale up for a larger-scale coating and does not require sophisticated apparatus.

## Experimental Section

### Reagents

The substrates used in this study, are industrial grade Cu, having a purity of 98%. The reagents used were Silver nitrate ( $\text{AgNO}_3$ ), perfluorodecyltriethoxysilane (PFDTES), ethanol, acetone, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydrochloric acid (HCL) and all of them are of analytical grade with the purity of 99% purchased from Sigma Aldrich, India.

PFDTES solution is used for surface hydrophobic modification of the prepared membranes. Hydrogen peroxide is used as a chemical etchant to modify the Cu substrate. The high thermal conductivity of Ag provides opportunities for its application in many heat transfer enhancement studies and the other method to apply silver onto substrates by means of colloidal silver particles. In most of the cases, silver can be

prepared in colloid by the reduction of dissolved silver nitrate. These solutions containing highly dispersed colloidal silver can be used as a liquid coating.

### Solution preparation

To modify the wettability of copper substrates, two-step dip coating technique has been used and it is very simple, requires less than two hours and which can be performed at ambient conditions without any special equipment. Several different solution concentrations were tested and evaluated in the dip-coating process, and thereafter, proper parameters were chosen. Two solutions were prepared for dip coating process as followed, the first solution consists of (0.5 M)  $\text{AgNO}_3$  aqueous solution and the second solution is a mixture of an ethanol solution containing (1 M) HCL and (1g) PFDTES.

### Deposition of $\text{AgNO}_3$ on Cu substrate

A schematic view and photographic view of dip coating equipment are presented in Fig. 1 (a) and (b) respectively. Initially, the substrates were polished using a surface polishing machine and the substrates were then ultrasonically cleaned at a frequency of 15 Hz in a soap solution for 10 min.

Three different methods such as 1) chemical etching, 2) mechanical rubbing and 3) combination of the above (mechanical rubbing chemical etching) were adopted separately to increase the roughness of the polished Cu substrate. Chemical etching of Cu substrate (CS1) was carried out in an aqueous solution of hydrogen peroxide kept in the ultrasonic bath for 15 min. In mechanical roughening, the Cu substrate (CS2) is gently rubbed with an abrasion sheet with different particle sizes of  $63\ \mu\text{m}$ ,  $35.8\ \mu\text{m}$ , and  $15.3\ \mu\text{m}$ . Another set of Cu substrate (CS3) was prepared using a combination of mechanical rubbing followed by chemical etching. In each case, all the three prepared substrates were cleaned ultrasonically using

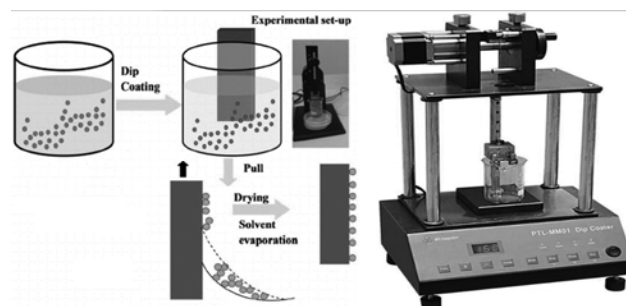


Fig. 1 (a) — Schematic view of dip coating process. (b) Photographic view of dip coating equipment

ethanol; acetone and distilled water and the substrates were kept in an oven for 10 min.

Dip coating was performed as follows: The coating was applied through two-step dip coating technique. Several different solution concentrations were tested and evaluated for the dip-coating process and thereafter, proper parameters were chosen. The prepared substrates were first immersed in 0.5 M aqueous solution of  $\text{AgNO}_3$  for 5 seconds and removed, 50 then followed by dipping in a solution mixture of ethanol, HCL, and PFDTES for 10 min. Afterwards, the substrates were placed in an oven at a temperature of  $100^\circ\text{C}$  for one hour to make them dry. The substrates were then characterized using different techniques as described in the following sections.

### Results and Discussion

The surface morphology of all the substrates was examined by scanning electron microscope (Tescon vega-3) and their roughness was measured by a surface profilometer (Talysurf-Cci Lite) as illustrated in Fig. 2. The presence of scratches and pits were noticed in the polished copper substrate (CS) with the roughness value of  $0.017\text{ }\mu\text{m}$  as shown in Fig. 2 (a). It is seen that the inherent closely packed grain structures in copper substrate resulted in lower roughness.

As depicted in Fig. 2 (b), the pits were irregularly placed with the larger size, than the polished copper

substrate due to chemical etching that leads to an increase in the roughness ratio of  $0.457\text{ }\mu\text{m}$  from  $0.017\text{ }\mu\text{m}$  for the etched copper substrate. During chemical etching, the Cu was etched with an aqueous solution of hydrogen peroxide. The Energy-Dispersive X-Ray Method (EDX) technique is used to determine the composition of a specimen as a whole as well as the composition of individual components. The inset shows an inspection field within which EDX data were collected by rastering the incident electron beam to produce the spectrum. From the Fig. 2 (c), the traces of rich in copper with a weight of 94.68%. The minimum amount of carbon with the weight of 3.43%, and oxygen with the weight of 1.89% are present on the substrate has been developed by the interaction between copper and chemical etchant.

When the etched substrate exposed to dip coating, leaf structure on the copper substrate was formed as shown in Fig. 2 (d) that leads to an increase in roughness value. The formation of the structure was mainly due to the presence of silver and functionalization with a low-surface-energy PFDTES. From the Fig. 2 (e), the tabulated results provide a view of the elemental composition in the inspection field in units of weight percent. The results reveal that Cu, Ag, O, F and Cl are the elements present in the inspection field, with Cu being the most abundant. From the EDX result, it is inferred that Ag presents on the Cu substrates after dip coating.

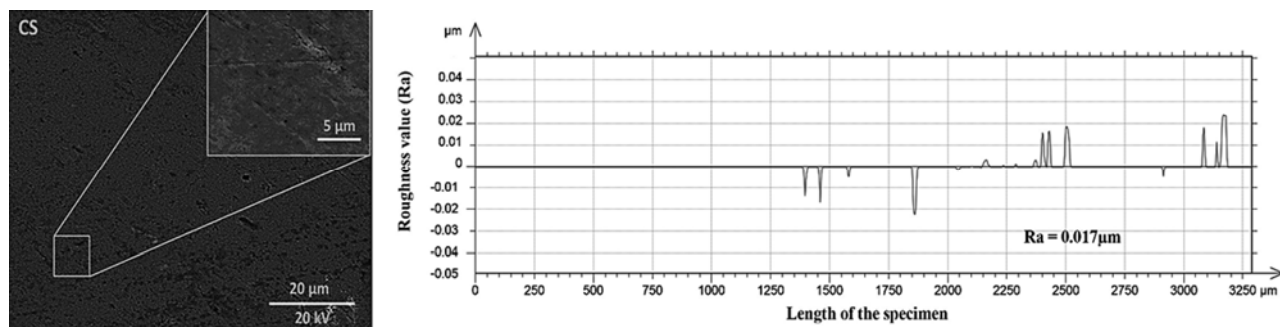


Fig. 2 (a) — SEM image and surface roughness image of polished Cu substrate.

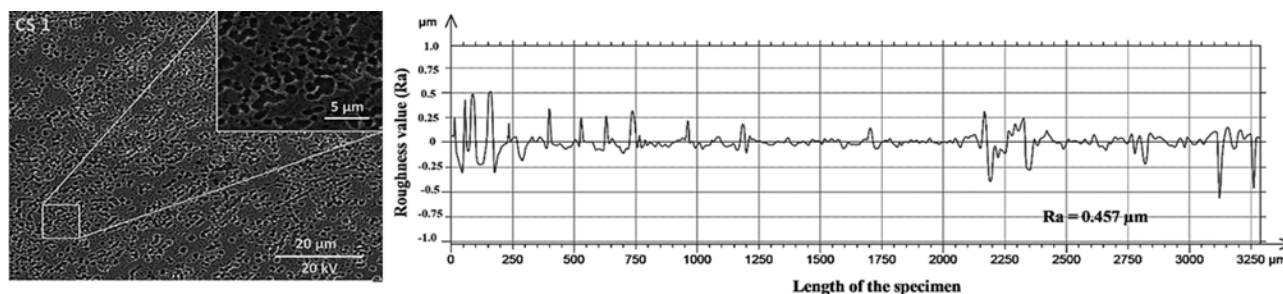


Fig. 2 (b) — SEM image and surface roughness image of chemically etched Cu substrate.

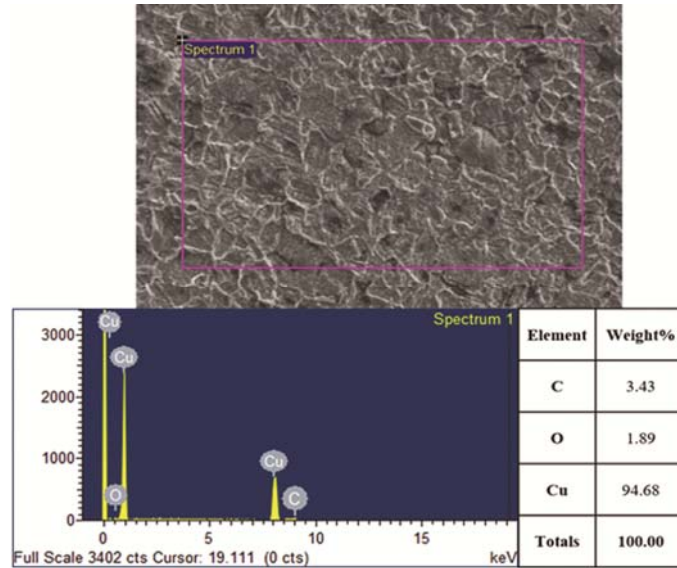


Fig. 2 (c) — EDAX image of elements present on Cu substrate after chemical etching

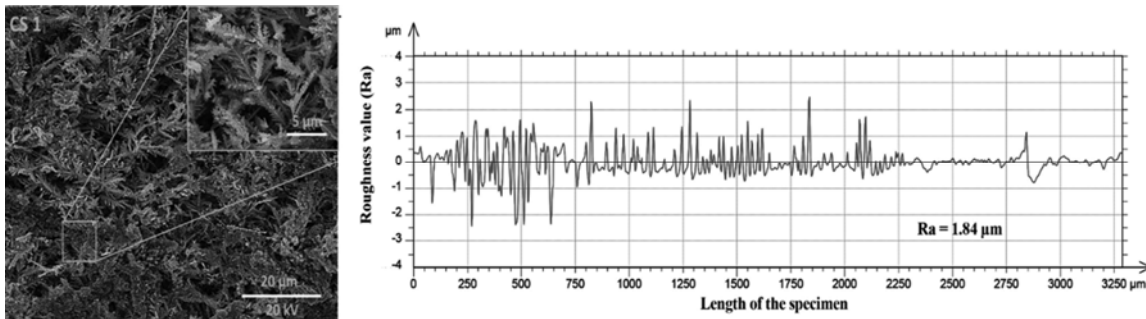
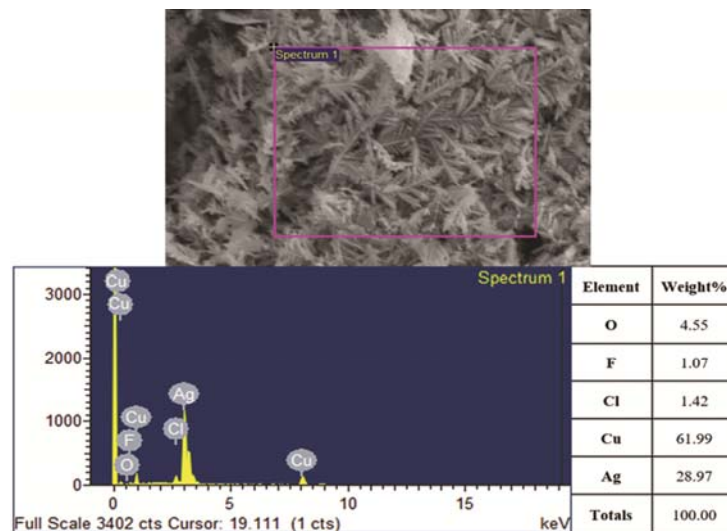
Fig. 2 (d) — SEM image and surface roughness image of  $\text{AgNO}_3$  coated Cu substrate after chemical etchingFig. 2 (e) — EDAX image of elements present in  $\text{AgNO}_3$  coated Cu substrate after chemical etching

Figure 3 (a) shows the surface modification of copper substrate obtained with mechanical rubbing and the roughness value is increased to  $0.281 \mu\text{m}$  due

to the existence of microgrooves, scratches and pits were noticed. By combining mechanical rubbing and etching, it is observed that the value of roughness

increased to  $0.602\text{ }\mu\text{m}$  for the copper substrate as shown in Fig. 3 (b). A similar increase in roughness along with dendrites and leaf structure on the copper substrate was achieved by mechanical rubbing followed by dip coating as shown in Fig. 3 (c). It is

interesting to note that the adoption of etching, mechanical rubbing, and dip coating resulted with the maximum increase of surface roughness as illustrated in Fig. 3 (d) that would be beneficial to fabricate the hydrophobic/superhydrophobic substrate.

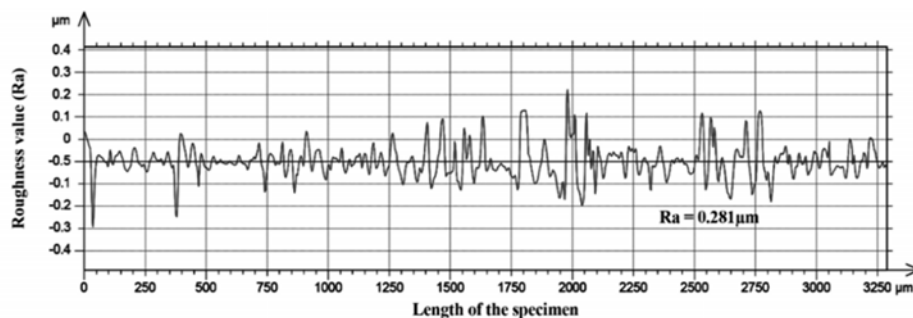
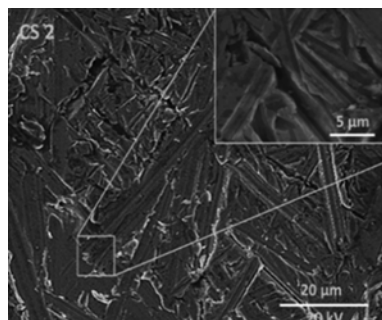


Fig. 3 (a) — SEM image and surface roughness image of mechanically rubbed Cu substrate

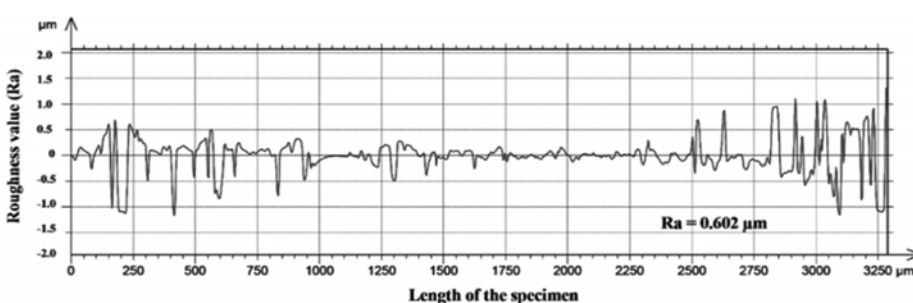
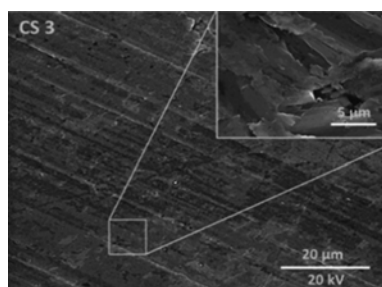


Fig. 3 (b) — SEM image and surface roughness image of the Cu substrate after chemical etching followed by mechanical rubbing

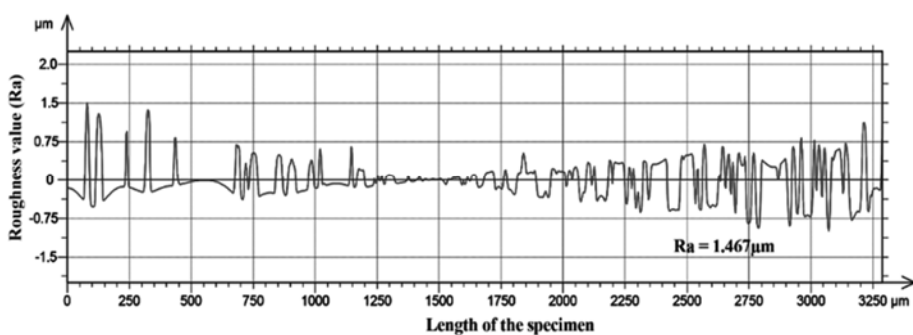
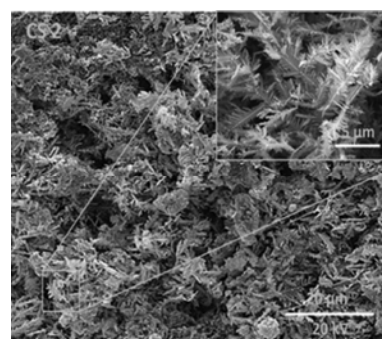


Fig. 3 (c) — SEM image and surface roughness image of  $\text{AgNO}_3$  coated Cu substrate after mechanical rubbing

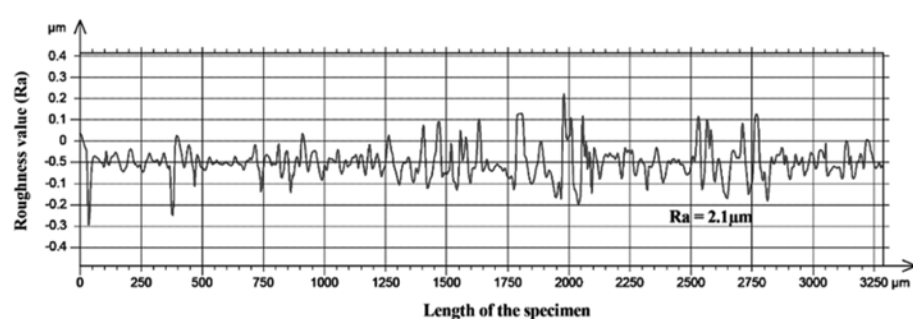
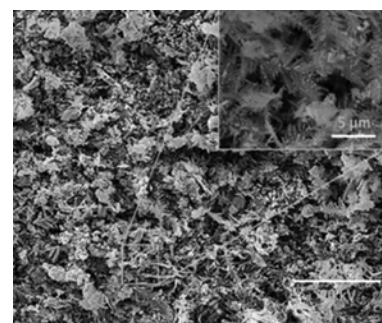


Fig. 3 (d) — SEM image and surface roughness image of  $\text{AgNO}_3$  coated Cu substrate after chemical etching followed by mechanical rubbing



A droplet size of 5  $\mu\text{L}$  was taken and the CA was computed at six different positions in a tester maintained at 30  $^{\circ}\text{C}$  temperatures. It is observed from Fig. 4 (a) that the contact angle of the polished copper substrate was found to be 92 $^{\circ}$  in 'CS'. The superhydrophobicity (contact angle of 150 $^{\circ}$ ) was not attained in Cu substrates by chemical etching, mechanical rubbing and combination of above as observed in Fig. 4 (b), this substrate that does not allow the water droplets to roll off easily.

However, the contact angle was increased due to the coating that forms the dendrites and leaf structures to trap air between them that enables the water droplet to roll off the substrate more easily. The corresponding contact angles are presented in Fig. 4 (c) and it lies in the range between 152 $^{\circ}$  to 160 $^{\circ}$ . From the above results, the substrate with PFDTES coating enhances the superhydrophobicity through the creation of microstructures and these structures are stable on the substrates due to the presence of siloxane bonds in PFDTES.

The hydrophobicity nature is increased gradually observed using contact angle measurement. Due to etching & rubbing, copper substrates behaves as hydrophobicity and does not allow water to roll off easily from the substrates are visually observed. The etching, rubbing followed by dip coating that forms dendrites and leaf structures to trap air between them that enables the water droplet to roll off the surface more easily compare to the etching & rubbing. The coated surface acts as a superhydrophobic surface.

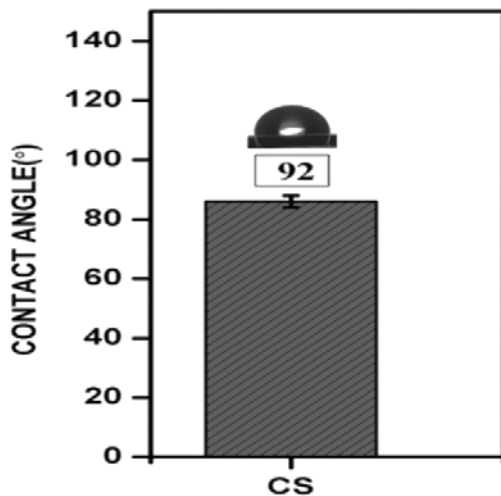


Fig. 4 (a) — Contact angle measurement of polished Cu substrate

The stability of the coating was analyzed under aging test, the test consisted of 30 days under ambient (30  $^{\circ}\text{C}$ ), low (5–10  $^{\circ}\text{C}$ ) and high temperature (105 – 110  $^{\circ}\text{C}$ ) conditions. It can be inferred from Fig. 5,

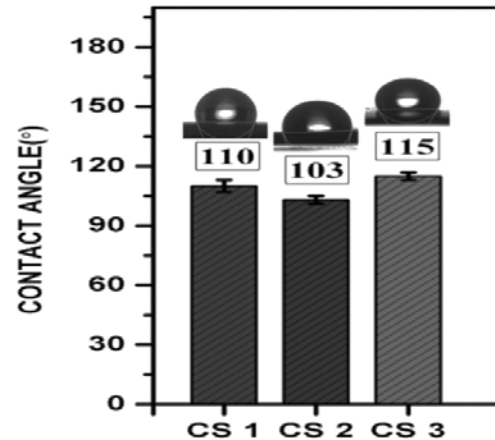


Fig. 4 (b) — Contact angle measurements of the Cu substrate after surface modifications. (Chemical etching (CS1), mechanical rubbing (CS2) and the combination of both (CS3)).

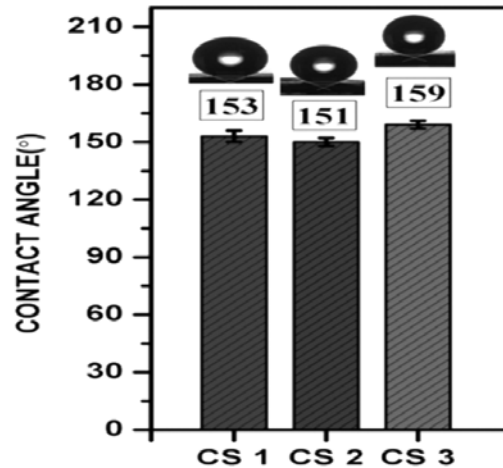


Fig. 4 (c) — Contact angle measurements of  $\text{AgNO}_3$  coated Cu substrate after surface modifications (Chemical etching+ coating (CS1), mechanical rubbing+ coating (CS2) and combination of the both+ coatings (CS3)).

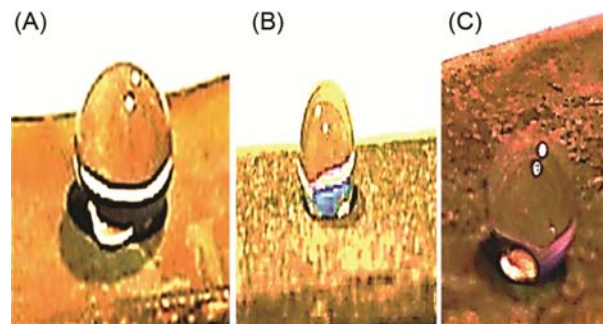


Fig. 5 — Hydrophobic nature of  $\text{AgNO}_3$  coated Cu substrate. (A) Ambient (B) low and (C) high temperature, respectively after 30 days

for all the temperature conditions the hydrophobicity nature Cu substrates remain unchanged. Based on the above discussion, it is concluded that the proposed coating method is the most beneficial in developing the superhydrophobic substrate even on substrates with the large surface area and complex geometry. Hence, the CA of coated substrates unchanged at different temperature conditions, these substrates can be used for heating (condensation heat transfer) applications.

### Conclusion

In summary, superhydrophobic surfaces have been successfully developed by a simple dip coating technique. Dip coated Cu substrate ( $\text{AgNO}_3$  coated Cu substrate) for all the temperature conditions in the stability test, the contact angle of  $\text{AgNO}_3$  coated Cu substrates remain unchanged. Dip coating method is the most beneficial in developing the superhydrophobic surface, even on substrates with the large surface area, complex geometry and minimal wastage of coating solution since any excess solution simply drips back into the dip tank that can be used in the next round of application. Hence, the contact angle of coated substrates unchanged at different temperature conditions, these substrates can be used for heating (CHT) applications which finds many applications in various energy-intensive sectors.

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